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NONCRYSTALLINE SEMICONDUCTORS: ELECTRICAL AND THERMAL PROCESSES

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Title: Noncrystalline Semiconductors: Electrical and Thermal Processes

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Principal Investigator and Project Scientist:

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FINAL REPORT

Noncrystalline Semiconductors: Electrical and Thermal Processes

I. Scope

The worldwide scientific quest for an understanding of the switching phenomenon in amorphous semiconductor films faced a controversy as to whether it was a thermal or electronic process. The first year of research on this project consisted in part of a comparison of experimental observations of switching in AsTe film with computer simulations of switching.[1] This comparison indicated that the switching observed (when repetitive voltage pulses were applied) was due to the conductance charges associated with repetitive heating and cooling of a micron-sized portion of the film. This work and research by others has quieted the controversy.

A practical concern about the stability of chalcogenide switching devices prompted switching studies in the more stable oxides. These include oxides from the $Bi_2O_3 \cdot ZnO \cdot MnO$ ternary system (section II) and the $V_2O_5 \cdot P_2O_5$ binary (section III). The switching in these oxides was predominantely of the memory type, which is due to the formation of crystalline ("ON" state) and noncrystalline ("OFF" state) phases. A basic study compared the electronic spectra, structures, and electrical characteristics of several crystalline and noncrystalline semiconductors. A new technique for the preparation of oxide films has been developed (section IV). Characterization of numerous other oxide films is progressing under an AROD grant.

A listing of the publications associated with this grant is included in Appendix I and the personnel associated with this research are described in Appendix II.

II. Switching Studies in $xBi_2O_3 \cdot yZnO$, zMnO

A. Introduction

Nonlinear I-V characteristics were observed in ZnO-Bi_2O_3 ceramics[2,3,4]. These ceramics consisted of conducting ZnO grains separated by an insulating grain boundary phase , a $ZnO \cdot Bi_2O_3$ glass or solid solution. When a voltage is applied to this ceramic, the greatest fields fall across the grain boundary phase which typically is about 600 Å thick. Then the current rises exponentially with voltage suggesting that the high fields on the grain boundary phase cause the resistivity to drop.

This phase of the research was undertaken in an effort to observe and characterize switching in oxide film similar to the grain boundary phase of $ZnO \cdot Bi_2O_3$ ceramics.

B. Procedure

Two compositions were studied: $86Bi_2O_3 \cdot 14ZnO$ ("BZ") and $70Bi_2O_3 \cdot 10ZnO \cdot 20MnO$ ("BZM"). The 86:14 ratio of Bi_2O_3 and ZnO corresponds to the eutectic composition in this system. The eutectic composition is the one most likely to form in the ZnO-Bi_2O_3 ceramic grain boundaries. MnO was added in an effort to enhance electrical conduction.

Solid polycrystalline BZ and BZM samples (1" diameter, 3/8" thick) were made by dry pressing and sintering at temperatures approaching the melting points of these oxides. Thin films were prepared by radio frequency sputtering. Electrical conduction was determined by the four-point probe technique and switch was studied as described for AsTe.

Electrical conductivity measurements of the BZ and BZM films revealed that the temperature dependence of conductivity was very unusual. It was a minimum (10^{-12} ohm-cm^{-1}) near room temperature and rose to 10^{-10} at 200°C and at 0°C.

No threshold switching could be observed. Computer simulation, using the conductivity versus temperature plot, reveal that the conductance rise would not occur using the experimental voltages. These observations indicate that the typical intrinsic exponential rise in conductance with increasing temperature must be present before switching can occur. This is further evidence that switching is a thermal phenomenon.

III. Switching Studies in $V_2O_5 \cdot P_2O_5$ Films

A. Introduction

Other oxides which would be expected to demonstrate typical intrinsic semiconductor characteristics (a linear log σ vs 1/T relation) would be the oxide semiconducting glasses, the best known being the $V_2O_5 \cdot P_2O_5$ glasses[5-10].

B. Procedure

Switching was studied in two compositions, $70V_2O_5 \cdot 30P_2O_5$ (VP1) and $60V_2O_5 \cdot P_2O_5$ (VP2). Since P_2O_5 is highly hydroscopic, it was introduced as orthophosphoric acid. This acid was mixed with V_2O_5 and some distilled water to form a slurry. The slurry was dried in an oven at 175°C until it attained a constant weight (approx. 40 hours). These reacted materials were melted in an alumina crucible with lids for 30 minutes. The molten glass was poured onto a 270°C steel plate and annealed at that temperature for eight hours, then allowed to cool to room temperature over another eight hour period by turning off the furnace. The glass plates were formed into sputtering target by a grinding operation. Films were deposited on aluminum electrodes and switching was studied.

C. Results and Discussion

Only occasional temporary appearances of threshold switching were observed in these $V_2O_5 \cdot P_2O_5$ glasses. However, a very reproducable memory switching behavior was observed. Switching studies on these glasses are continuing. VP2 has a conductivity-temperature relationship very similar to AsTe, except that it was an order of magnitude more resistive. VP1 has a positive temperature coefficient of resistance and switching would not, therefore, be expected.

IV. Pyrolytic Deposition of Oxide Thin Films

In the foregoing work on oxide films, it was found that sputtering and evaporation deposition techniques provided films which were oxygen deficient and therefore were extrinsic semiconductors. The experience of this research indicates intrinsic conduction is a necessary, but not a sufficient, requirement for threshold switching. This indicated that the oxide films should be fully oxidized so that they would be intrinsic, but still have a significant room temperature conductivity (e.g. $\sim 10^4$ $(\text{ohm}\cdot\text{cm})^{-1}$). This lead to the deposition of oxide films in an infinite supply of oxygen, that is by the pyrolitic decomposition of various salts dissolved in alcohol or water. The conventional pyrolytic deposition of oxide films usually involves heating the substrates to $\sim 650^{\circ}C$, a temperature much too high for the metal substrates used in the switching studies. A new technique was developed which allows deposition to occur at $\sim 300^{\circ}C$. A paper describing this technique has been submitted to the American Ceramic Society for publication and is included in Appendix III. Deposition of numerous oxide films and their electrical evaluations are being continued under an AROD grant.

REFERENCES

1. W. D. Leahy and L. H. Slack, "Computer Simulation and Experimental Studies of Switching in AsTe Films," presented at the Fifth International Conference on Amorphous and Liquid Semiconductors, at Partenkirchen-Garmish, Germany, on Sept. 3, 1973. Being published in the proceedings of the conference by the North Holland Publishing Company.

2. M. Matsuoka, T. Masuyama and Y. Iida, "Nonlinear Electrical Properties of Zinc Oxide Ceramics," Japan J. Appl. Phys., Suppl. 39, 94-101 (1970).

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4. W. G. Morris, "Electrical Properties of ZnO-Bi_2O_3 Ceramics," J. Am. Ceram. Soc., 56 (7) 360-364 (1973).

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10. B.V.J. Rao, "Structure and Mechanism of Conduction of Semiconductor Glasses," J. Am. Ceram. Soc., 48 (6), 311 (1965).

APPENDIX I

Publications of Research Based on this Grant

A. Publications in Print

1. A. Rohatgi, T. Viverito, and L. H. Slack, "Electrical and Optical Properties of Tin Oxide Films," J. Am. Ceram. Soc. 57 (6) 1974 (Partial ARPA Support).

2. M. P. Shaw, S. C. Moss, S. A. Kostylev, and L. H. Slack, "Pre-switching and Post-switching Phenomena in Amorphous Semiconducting Films," Appl. Phys. Lett., 44 (3) 114-117, 1973. (Note: S. A. Kostylev was an exchange scientist from the Soviet Union for three months here and three months at Wayne State University.)

B. Publications in Press

1. W. D. Leahy and L. H. Slack, "Computer Simulation and Experimental Studies of Switching in AsTe Films," presented at the Fifth International Conference on Amorphous and Liquid Semiconductors, at Partenkirchen-Garmish, Germany, on Sept. 3, 1973. Being published in the proceedings of the conference by the North Holland Publishing Company.

2. L. H. Slack and L. R. Durden, "Observation of Electronic Spectra in Glass and Ceramic Surfaces," presented at the "Surfaces and Interfaces of Glasses and Ceramics" Conference at Alfred University, Alfred, New York, on August 27, 1973. Being published in the proceedings of the conference by Plenum Press.

C. Publications in Preparation

1. Temperature Dependence of Conductions as Related to Switching in Oxide Thin Films.

2. Electronic Spectra in Amorphous and Crystalline Ge_xTe_y and Ge_xSe_y.

3. Conduction and Electronic Spectra in Several Amorphous and Crystalline Semiconductors.

APPENDIX II

Graduate Students

Name, Degree	Thesis Title	Current Status
C. L. Hackler, M.S. Ceramic Engineering (Partial Support from ARPA)	"Reactive Radio Frequency Sputtering of Iron Oxide Thin Films for Electrical Resistivity Characterization", accepted May 1974.	Ceramic Engineer Pemco Division of Glidden-Durkee Corp., Baltimore, Md.
L. R. Durden, Ph.D. Materials Engineering Science	"Electrical Characteristics and Basel Structure of Crystalline and Amorphous Semiconductors", to be defended Summer 1974.	Assistant Professor University of Kentucky Ashland Community College, Ashland, Ky.
W. D. Leahy, M.S. Ceramic Engineering	"Computer Simulation and Experimental Studies of Switching in AsTe Films", to be defended Fall 1974.	Ceramic Engineer, Corning Glass Works Corning, New York
M. D. Chakraborty, M.S. Ceramic Engineering (Partial Support from ARPA)	"Electronic and Ionic Conduction in $V_2O_5 \cdot P_2O_5$ Glasses," in process.	Graduate Student

APPENDIX III

Oxide Film Deposition by an Improved Pyrolitic Decomposition Process

With the proliferation of oxide thin films for optical and electrical applications, the controlled pyrolitic deposition of oxides is of widespread interest, especially in cases where vacuum deposition of oxides is impractical or uneconomical. The conventional pyrolitic process consists of spraying a salt solution onto a heated substrate at which the solvent evaporates, the salt decomposes and the salt's cation combines with atmospheric oxygen to form the oxide film on the substrate. When the salt decomposition and subsequent oxidation provides a negative free energy change, the oxide film is formed; otherwise none is formed.

The conventional pyrolitic deposition of oxide films[1,2,3,4] consists of spraying a dilute solution of a metal salt from a corrosion-resistant spray gun onto the heated substrate. The improved method consists of dispersing the solution into micron and submicron sized droplets to form a fog using the glass apparatus shown schematically in Figure 1. The solution is pumped, using a conventional circulating tubing pump, so that it runs

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1. A. Rchatgi, T. K. Viverito, and L. H. Slack, "Electrical and Optical Properties of Tin Oxide Films", J. Am. Ceram. Soc. 57 (7) 1974.

2. R. Gomer, "Preparation and Some Properties of Conducting Transparent Glass", Rev. Sci. Instru., 24 993, 1953.

3. V. K. Miloslavskii, "Infrared Absorption of Thin Films of Tin Dioxide", Opt. Spectr. (USSR) English Translation, 1, 154, 1959.

4. C. A. Vincent and D. G. C. Weston, "Preparation and Properties of Semiconducting Polycrystalline Tin Oxide", J. Electrochem. Soc., 119 519-521, (1972).

over a hollow glass sphere (A). That sphere has a tiny slit (0.006 in. wide) through which air is blowing. This small flow of air causes the thin sheet of solution flowing down over the sphere to be dispersed into a fog[5]. Two obstructions, a glass ball (B) and a rise in the tube (C) tend to trap the larger droplets which return to be recycled with the undispersed solution. The fog is guided by the glass tube to the heated substrate, where pyrolytic decomposition and oxide formation occurs.

TABLE I

Comparison of the new and conventional processes spraying a 2.85 M $SnSl_4 \cdot 5H_2O$ alcohol solution to provide a SnO_2 film

	Substrate Temp. (°C)	Air Flow Rate (cfm)	Spray Time(sec)	Cooling After: 10 sec.	60 sec.
New	350	0.60	240	57°C	65°C
Conventional	650	5.0	15	95°C	163°C

	Thickness Å	Resistivity (Ωcm)
New	1034	0.05
Conventional	1391	0.05

5. S. Dresner, "It's Superspray", Popular Science, p. 102, May (1973).

A comparison of the conventional and new processes has been made using a 2.85 M $SnCl_4 \cdot 5H_2O$ solution to deposit SnO_2 films. The results of this comparison are summarized in Table I. The lowest substrate temperatures consistent with good film deposition were used. The most striking difference between the conventional sprayer and the fog generator is the difference in the lowest substrate temperature that could be used to provide quality tin oxide films. The very high flow rate required by the conventional sprayer causes considerable cooling during the first seconds of spraying. Therefore, the substrates must be heated about 300°C above that used with the fog generator in order to maintain the substrate above the minimum deposition temperature throughout the entire spraying cycle.

The electrical sheet resistance of the tin oxide films were essentially the same. The optical properties were also similar except that the film deposited with the fog generator was more intensely colored (yellow) even though it was slightly thinner.

The low air flow rate used with the fog generator leads to other advantages. The fog is easily contained and guided to the substrate where it completely reacts. There is little waste of material and the operator and equipment are not exposed to the spray. The film thickness could be controlled with precision by automatically controlling the time that the tubing pump was running. Film uniformity was also improved using the fog generator in these laboratory experiments.

The glass construction facilitates clean-up and eliminates the corrosion problems encountered in metal sprayers using some solutions.

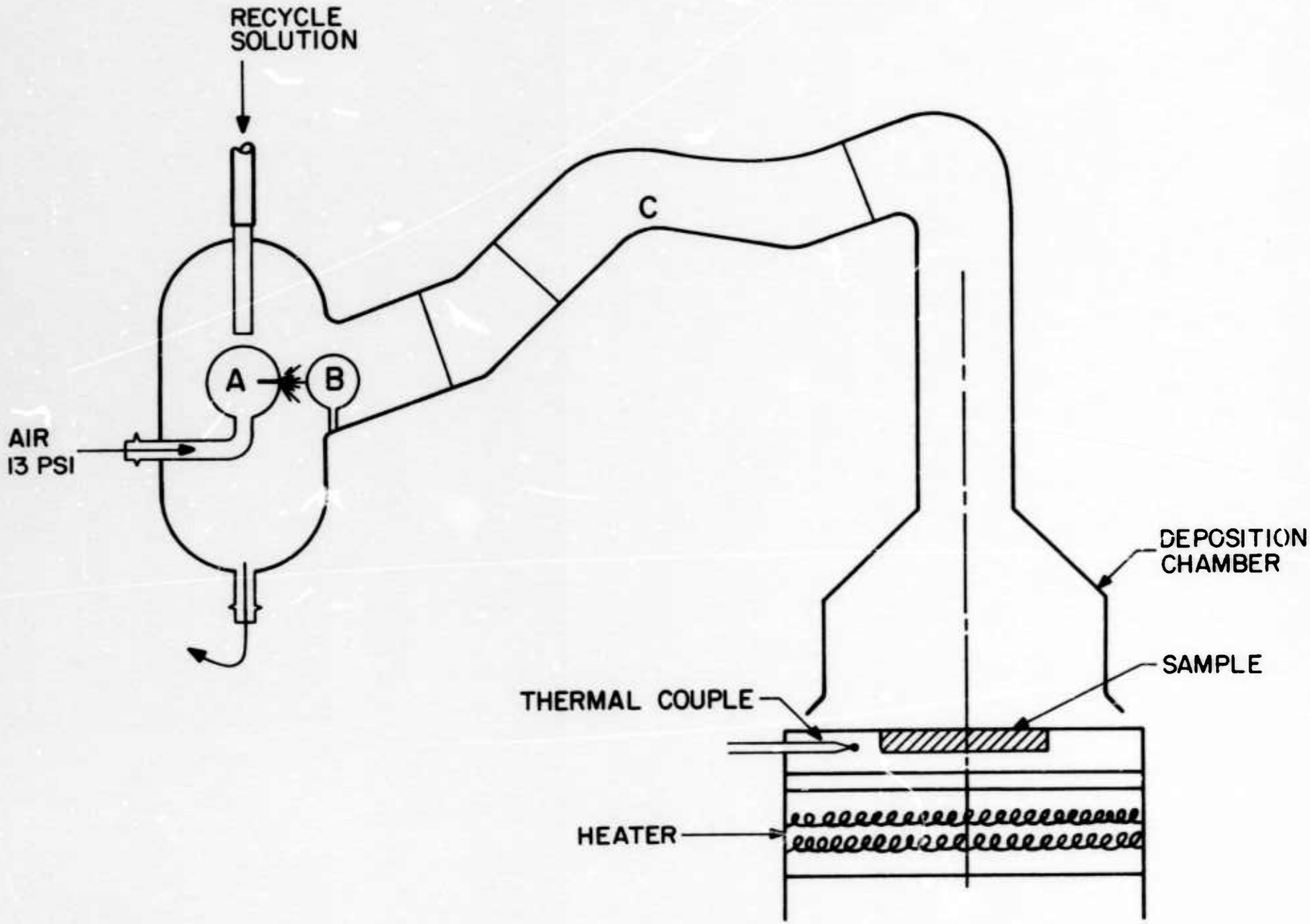

FIG. 1. SCHEMATIC DIAGRAM OF THE IMPROVED PYROLITIC SPRAYING PROCESS.